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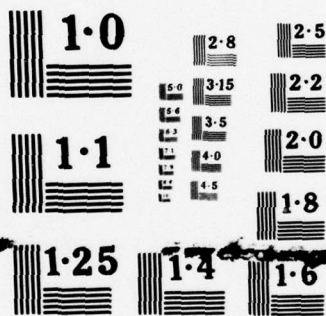   OCT 77   DNA001-75-C-0023
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MICROCOPY RESOLUTION TEST CHART

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This issue of the DASIAC Reaction Rate Data presents summaries of recent progress in investigations supported by the Defense Nuclear Agency in portions of its Reaction Rate Program, plus summaries of related work submitted by other non-DNA-funded investigators. Formal DNA reports (where indicated) may be purchased from the Defense Documentation Center, Cameron Station—Building 5, Alexandria, Virginia 22314; or the information contained in such reports may be obtained from articles published in scientific and technical journals.

The major portion of this document is composed of informal, bimonthly technical progress reports comprising information and data which are preliminary in nature and may be subject to future revision and/or changes. It is requested that recipients do not cite or reference the contents of this issue in other media without prior approval by the author and organization involved. This professional courtesy is greatly appreciated by all contributors, especially those who intend to publish formally elsewhere at a later date.

Technical progress reports and other information for publication in future editions of the DASIAC Reaction Rate Data are welcome, and should be sent to: DASIAC, Attn. D. Reitz, General Electric Company—TEMPO, 816 State Street, Santa Barbara, CA 93102. DASIAC is DOD-approved and contractually engaged by DNA for this purpose.

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PART I – DNA-SPONSORED RESEARCH
Progress through August 1977

A.   SUBTASK S99QAXHD411

"Reaction Rates Essential to Propagation."

1.   Applications of the AIRCHEM Computer Code–F. Niles, J. Heimerl, AASLNM (Work Unit 01).

Manuscripts are being prepared that detail the input and output of the BENCHMARK-76 program. The three BRL Reports are titled "BENCHMARK-76: Model Computations for Disturbed Atmospheric Conditions. I. Input Parameters," ". . . II. Results for the Stratosphere and Mesosphere," and ". . . III. Results for Selected Excitation Parameters at 60 km."

Two other manuscripts are in preparation for BRL reports: "SOURCE: A FORTRAN-IV Subroutine Package that Models Several Naturally Occurring Energy Inputs to the Mesosphere" by I. L. Chidsey specifies the solar, cosmic ray and precipitating electron inputs to the mesosphere and stratosphere, and "Output Routines for Time-Dependent Solutions to Multispecies Reaction-Chemistry Codes" by I. L. Chidsey and E. L. Lortie details the output routines used in the AIRCHEM chemistry code.

Three BRL memorandum reports have been published: "On the Units of the Equilibrium Constant" by J. M Heimerl (No. 2758), "Selected Neutral Species Profiles, 0-100 km" by F. E Niles and J. M. Heimerl (No. 2767), and "Comments on the Solution of Coupled Stiff Differential Equations" by M. D. Kregel and J. M. Heimerl (No. 2769).

The $NO^+(NO)/NO^+(SO_2)$ note by J. A. Vanderhoff and J. M. Heimerl has been published in J. Chem. Phys. <u>66</u>, 3838-3840, 1977.

2.   Positive-Negative Ion Reactions in Various Atmospheric Gases–J. Vanderhoff, BRL (Work Unit 02).

Further investigations have been conducted on the photodissociation cross section of CO_3^-. By varying the O_2/CO_2 gas mixture CO_3^- can be formed either by the reaction $O^- + CO_2 + O_2 \rightarrow CO_3^- + O_2$ or $O_3^- + CO_2 \rightarrow CO_3^- + O_2$. Photodissociation cross section measurements of CO_3^- formed either from O^- or O_3^- yielded essentially the same results. It has been noted in the last report that the photodissociation cross sections measured for CO_3^- were typically within 25% of those obtained by Crosby *et al.* We obtained those data for conditions where the O_2/CO_2 gas mixture was approximately 395 mTorr O_2 and 5 m Torr CO_2 and at an E/N of 15 Td. More recently we have obtained photodissociation cross sections for CO_3^- of a smaller magnitude when using a gas mixture of 399 mTorr O_2 and 1 mTorr CO_2 and an E/N of 5 Td. For a fixed photon wavelength a pressure and E/N dependence was also observed. Further investigation of CO_3^- is planned.

SO_4^+ produced in a O_2/SO_2 gas mixture exhibited a large photodissociation cross section, attaining values of approximately 1×10^{-17} cm^2 over the photon wavelength range of 670-570 nm.

BRL Report No. 1944 entitled "Photodissociation of $[NO^+(NO)]$ and $[NO^+(H_2O)]$" by J. A. Vanderhoff, July 1977, has just been published.

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3. *Electron and Cluster Ion Recombinations and Temperature Coefficients*—M. Biondi, R. John-sen, *and W. Whitaker, University of Pittsburgh (Work Unit 03).*

Electron-Ion Recombination Studies

The new copper and stainless steel microwave cavity has performed well in studies of the electron temperature dependence of recombination between electrons and hydronium series ions, $[H_3O^+ \cdot (H_2O)_n]$, with n = 0, 1, 2, 3 . . . As was first hinted at in studies of the hydronium cluster ions over a very limited temperature range and then confirmed in wide T_e range (300-3000 K) studies of ammonium series ions, $[NH_4^+ \cdot (NH_3)_n]$, ions to which polar molecules are clustered exhibit an un-usually weak dependence of the recombination coefficient α on T_e. In the case of hydronium cluster ions studied over the range 300 K $<$ T_e $<$ 6000 K, 73^+ (n = 3) exhibits a $T_3^{-(0.0\pm0.1)}$, 55^+ (n = 2) a $T_e^{-(0.1\pm0.1)}$, and 37^+ a slightly stronger inverse dependence on T_e. For the higher hydrates (n $\geqslant$ 4) it is difficult to establish individual dependences of α on T_e, but qualitatively a T_e^{-0} variation charac-terizes the equilibrium mixtures for $4 < n < 7$. In the coming months these studies will be completed and readied for publication.

Ion Molecule Reaction Rates

Studies with the high temperature drift tube are quite difficult, but progress, though slow, is being made on the $O^+ + N_2$ and $O^+ + O_2$ atom and charge transfer reaction studies over the tempera-ture range 300 K—1000 K.

4. *Positive Ion-Negative Ion Recombination Rate Coefficients for the Lower D Region*—J. Peter-son, *SRI International (Work Unit 06).*

Ion-ion rates were measured in the flowing afterglow apparatus in Birmingham, England, and a new ion source for producing complex molecular ion beams was designed.

T. M. Miller with M. J. Church and D. Smith at Birmingham made measurements on negative ions from species whose attachment rate is quite high so that ion-ion plasmas of high density can be formed. With the exception of SF_6^-, the negative ions have all had high electron affinities (EA $\geqslant$ 2.5 eV). With this limitation, attempts are being made to discover any systematic characteristics of the ion-ion reaction between relatively simple species and clustered ions. Recently the reactions of ions $[NH_4^+(NH_3)_n]$ with NO_2^-, Cl^- and $[NO_3^-(HNO_3)_n]$ with n = 0, 1, 2, have been studied. Prelimi-nary data for $[NH_4^+ \cdot (NH_3)_3] + Cl^-$ give 1.1×10^{-7} cm³/sec. This is larger than previous results for other ions obtained on that apparatus. The reaction rates are fairly uniform and in the range 7–9 x 10^{-8} cm³/sec at 300 K. They show a nearly $T^{-\frac{1}{2}}$ dependence between 180 and 530 K, which is also expected for atoms, and thus may indicate that in this limited temperature range, changes in initial internal energy do not alter the rates substantially. Since the rates remain the same, the cross sections of the clustered ions must increase roughly as the square root of the mass in order to offset the re-duced orbiting times, as is expected qualitatively from induced excitation of internal rotational and vibrational modes.

A preliminary value of 9.5×10^{-8} cm³/sec has been determined for the $O_2^+ + CO_3^-$ reaction (300 K). This rate is the largest measured so far in Birmingham, and it will be studied further.

The $NO^+ + NO_2^-$ reaction rate at 300 K is being reinvestigated and the results (6.3×10^{-8} cm³/sec) are essentially in agreement with previous Birmingham results.

T. Miller will continue to work in England during September. Additional temperature-depen-dent measurements will be made on $NO^+ + NO_2^-$, the possibilities of excited states will be examined, and other appropriate species will be studied. He is now formulating an assessment of the comparative capabilities of the flowing afterglow experiment and its possibilities for future work.

Plans for the ion source were adapted from the design of Searcy and Fenn, who have successfully formed cluster ions and injected them into a quadrupole mass analyzer, using a supersonic jet to aid in cooling and stabilization. The problem is to find a way to adapt their ideas to produce an ion beam, ultimately in a high vacuum, without heating up the ions, and with sufficiently good emittance characteristics (current and collimation) to permit ion-ion and photo-ion experiments. Work on the supersonic nozzle ion source is now nearly completed. Testing will be carried out using the merged-beams apparatus for the diagnostics when the fabrication is completed.

5. *E and F Region Rate Coefficients for Complex Negative and Excited Positive Ions—J. Paulson and E. Murad, AFGL (Work Unit 07).*

Because of continued interest in the photodissociation of clustered ions a molecular beam ion source was designed. In this source, ionization will occur in the gas at high pressure, and the ionized gas will then be expanded through a small orifice, where clustering occurs. Pumps and other equipment for this device have been ordered. Photodissociation of N_2O^+ at visible wavelengths has been reported (R. C. Dunbar, J. Am. Chem. Soc. 93, 4354 (1971) and A. Carrington, D. R. J. Milverton, and P. J. Sarre, Mol. Phys. 32, 297 (1976)). A series of measurements was made to determine upper limits for the cross sections. They were found to be $\sim 1 \times 10^{-20}$ cm^2 at 445 nm and $\sim 1 \times 10^{-21}$ cm^2 at 640 nm, both measurements referring to the process $N_2O^+ \rightarrow NO^+ + N$. The previously reported value was $\sim 2.5 \times 10^{-19}$ cm^2 at 625 nm (Dunbar).

The apparatus used for the measurements includes a quadrupole mass filter utilized both to mass analyze the product ions and as a time-of-flight (TOF) device. In addition to measurements of the absolute photodissociation cross sections, the apparatus can be used in the TOF mode to determine the translational energy distribution of the product ions and thus to infer the vibrational energy levels of the product ions. It was found that in the case of N_2O^+ photodissociated at 338 nm, the vibrational population of the NO^+ product ions is strongly inverted, with the $v = 6, 7, 8$ levels being most highly populated.

Although the collisional dissociation cross sections for CO_3^- have been measured, attempts to make similar measurements for $[CO_3^- \cdot H_2O]$ and $[NO_3^- \cdot H_2O]$ have so far been unsuccessful because of low available beam currents and interfering reactant ions at nearby mass-to-charge ratios. To alleviate both of these problems, the inlet system was rebuilt and a different ion source was installed. Experimental work will soon resume. The double mass spectrometer was modified in order to be able to heat N_2 to about 2200 K. A power supply for the Knudsen cell heater was ordered, received, and connected to the cell heater. A gas inlet molybdenum Knudsen cell has been designed and it is being fabricated. It is expected that this cell will be received shortly.

6. *Laboratory Measurements of Selected D-Region Reactions—F. Fehsenfeld, E. E. Ferguson, A. L. Schmeltekopf, C. J. Howard, and D. L. Albritton, NOAA (Work Unit 08).*

Current atmospheric models predict significant concentrations of H_2CO in the stratosphere as by-products of the oxidation of methane. For this reason the reactions

1) $[H_3O^+ \cdot (H_2O)_n] + H_2CO \rightarrow [H_3CO^+ \cdot (H_2O)_n] + H_2O$
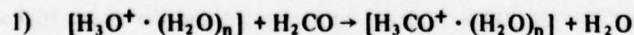
have been studied for $n = 0, 1, 2, 3$, in the variable temperature flowing afterglow. From these measurements thermochemical values for reactions 1) have been obtained. The results are as follows:

Reaction	ΔH_T^O	ΔS_T^O	Mean Temperature
	(K cal/mole)	(cal/mole K)	(K)
1a) $H_3O^+ + CH_2O \rightarrow CH_2OH^+ + H_2O$	-5.2±0.8	2.2±3.0	470
1b) $[H_3O^+ \cdot H_2O] + CH_2O \rightarrow [CH_2OH^+ \cdot H_2O] + H_2O$	-0.41±0.29	2.6±2.5	400
1c) $[H_3O^+ \cdot 2H_2O] + CH_2O \rightarrow [CH_2OH^+ \cdot 2H_2O] + H_2O$	0.58±0.43	2.3±2.8	400
1d) $[H_3O^+ \cdot 3H_2O] + CH_2O \rightarrow [CH_2OH^+ \cdot 3H_2O] + H_2O$	1.1 ±0.6	4.1±2.0	325
2) $[CH_3O^+ \cdot H_2O] + CH_2O \rightarrow [CH_2OH^+ \cdot CH_2O] + H_2O$	-0.80±0.13	-0.71±2.2	400

These measurements imply that the reactions of the hydrated hydronium ions with CH_2O in the stratosphere will not produce significant CH_2OH^+ and its clusters because of the small equilibrium constants and the large $[H_2O]/[H_2CO]$ ratio.

The conversion of O_2^+ and H_2O to H_3O^+ and $[H_3O^+ \cdot H_2O]$ plays an important role in the production of $[H_3O^+ \cdot (H_2O)_n]$, $n = 0, 1, 2, \ldots$, which are observed to be the dominant ions in the lower mesosphere and upper stratosphere. As a consequence, any reaction that could alter this process would be important to the ion chemistry below 80 km. In this connection, the reactions of O_2^+ and $[O_2^+ \cdot O_2]$ with CH_4, CO_2, and O_3 and the reaction of $[O_2^+ \cdot O_3]$ with H_2O have been investigated using the variable temperature flowing afterglow and the flow drift tube.

The reaction

$$O_2^+ + CH_4 \rightarrow CH_3O_2^+ + H \tag{1}$$

is found to be slow; $k_1 = 7.5 \times 10^{-12}$ cm^3 sec^{-1} at thermal energies. Because the reaction rate constant is slow this reaction will not be significant in the atmosphere.

The reaction

$$[O_2^+ \cdot O_2] + CH_4 \rightarrow CH_3O_2^+ + O_2 \tag{2}$$

is found to have a rate constant of $k_2 = 3.0 \times 10^{-12}$ cm^3 sec^{-1} at 140 K. Because the reaction rate constant is small, this reaction will not effectively compete with the reaction of $[O_2^+ \cdot O_2]$ with H_2O.

While neither CO_2 nor O_3 undergo binary reactions with O_2^+, $[O_2^+ \cdot O_2]$ switches with both neutrals. Equilibrium constants for the reactions

$$[O_2^+ \cdot O_2] + CO_2 \rightleftharpoons [O_2^+ \cdot CO_2] + O_2 \tag{3}$$

$$[O_2^+ \cdot O_2] + O_3 \rightleftharpoons [O_2^+ \cdot O_3] + O_2 \tag{4}$$
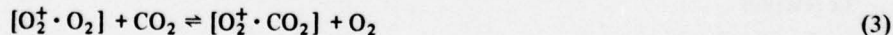
have been measured as a function of temperature. It was found that $-\Delta H_{273}^O$ (3) = -0.308 ± 1.0 kcal mole^{-1}, ΔS_{273}^O (3) = 4.3 ± 3.0 cal mole^{-1}K^{-1} while $-\Delta H_{273}^O$ (4) = 3.7 ± 1.0 kcal mole^{-1} and ΔS_{273}^O (4) = 4.5 ± 4.0 cal mole^{-1}K^{-1}. These equilibrium constants indicate that the concentration of $O_2^+ \cdot CO_2$ would be negligibly small relative to $[O_2^+ \cdot O_2]$ in the atmosphere, while the concentration of $[O_2^+ \cdot O_3]$ relative to $[O_2^+ \cdot O_2]$ would depend strongly on the O_3 to O_2 mixing ratio and temperature.

Finally the reaction

$$[O_2^+ \cdot O_3] + CH_4 \rightarrow products \tag{5}$$
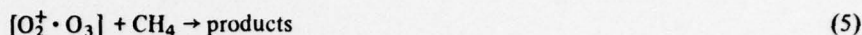
was studied at 230 K. Reaction (5) was found to be quite slow; $k_5 < 5 \times 10^{-13}$ cm^3 sec^{-1}. On the other hand, the reaction

$$[O_2^+ \cdot O_3] + H_2O \rightarrow [O_2^+ \cdot H_2O] + O_3 \tag{6}$$

is fast; $k_6 = 1.2 \times 10^{-9}$ cm^3 sec^{-1} with the measurements made at 260 K. Therefore, the formation of $[O_2^+ \cdot O_3]$ from $[O_2^+ \cdot O_2]$ will not alter the conversion of O_2^+ and H_2O to $[H_3O^+ \cdot (H_2O)_n]$.

7. *Low Energy Cross Sections for Debris Metal Ions–R. Neynaber, J. A. Rutherford, D. A. Vroom, IRT (Work Unit 10).*

The objective of the experimental program is to remeasure the charge transfer cross section for the reaction

$$N^+ + O \rightarrow N + O^+ \tag{1}$$
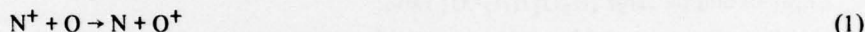
in the low energy regime (0.5 to 5 eV). The previously established upper limit for the cross section was 5×10^{-17} cm^2 at 5 eV[1]. The importance of this reaction has prompted another investigation. It has been established that the cross section for reaction (1) is probably much smaller than 2×10^{-17} cm^2 in the energy region considered.

The highest possible dissociation of the O_2 used in the neutral beam source is desirable. Most of the work has been done using a 50 MHz radio frequency power supply to produce a discharge in gas mixtures held inside a 20 mm U-shaped pyrex tube. Various mixtures of oxygen, hydrogen, and water have been used. The maximum degree of dissociation was obtained using a gas mixture of equal parts of O_2 and He with 2% H_2O vapor added and with a total pressure in the discharge tube of 300 millitorr. The neutral beam of O and other species is formed by effusion from a small hole in the outside of the center of the U bend. Care must be exercised when measuring dissociation fractions, as the value obtained for the number of O atoms in the beam may depend on the method of observation. For example, the number of O atoms in the beam may be determined by observing the O_2^+ formed in the reaction

$$N^+ + O_2 \rightarrow N + O_2^+ \tag{2}$$

(decreases in the O_2^+ are related to the amount of O formed) or from the appearance of a signal for the reaction

$$H^+ + O \rightarrow H + O^+ \tag{3}$$
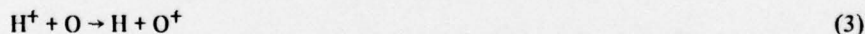
and from the known cross section for this reaction.[1] Under similar conditions, these two methods for obtaining the number of O atoms formed in the discharge often differ, with observation of Reaction (3) giving the lower value. The observation of Reaction (3) is used as a standard by which to establish beam density.

[1] J. A. Rutherford and D. A. Vroom, "The Reaction of Atomic Oxygen with Several Atmospheric Ions," J. Chem. Phys. 61, 2514 (1974).

One of the main problems in measuring the cross section for Reaction (1) (apart from obtaining a suitable O atom beam) is that the reaction probability appears to be very small. On the other hand, the cross section for the process

$$N^+ + O_2 \rightarrow NO + O^+ \tag{4}$$

is of the order of 2×10^{-17} cm^2 in the low energy regime. If there is any O_2 present in the neutral beam, production of O^+ by Reaction (4) tends to obscure any signal due to Reaction (1).

There are two ways to circumvent the problem described: get a higher dissociation fraction in an O_2 mixture or use a source of O atoms other than O_2. The highest dissociation fraction obtained was 25%. Measurements were also done using CO_2 with a trace of H_2O in the discharge to produce the O atoms. In the energy range from 1.8 to 10 eV, measurements with both systems of O generation gave (after all corrections are made for beam density changes) the cross section for Reaction (1) in the energy range below 4 eV as less than 2×10^{-17} cm^2.

In an attempt to improve on these measurements, a microwave discharge source has been constructed. This cavity is of the Evenson type but has been modified to fit in the restricted volume of the neutral beam source chamber. The cavity operates at 2450 MHz and is powered by a 100 watt Raytheon Microtherm unit. Testing of this cavity is now underway. Coupling through the vacuum wall was accomplished with type N connectors. The microwave power was conducted from this connector to an Evenson type cavity using semi-rigid coaxial cable.

The microwave cavity worked well from the outset but had a problem in that it produced a significant number of high energy photons which created a large coherent noise signal. This problem was severe when the microwave cavity was near the exit of the atom source but was significantly reduced when it was moved back such that it was out of the line of sight of the neutral beam. With both the rf source used previously and the microwave cavity, the amount of dissociation obtained was greatly increased by coating the tube with phosphoric acid. The dissociation fraction obtained was similar with both types of discharge source. The results indicated that fewer metastable states were created by the more diffuse rf discharge, and there is less heating of the quartz tube with a resultant increase in the lifetime of the phosphoric acid coating. These observations have resulted in the choice of the rf source. With this source and the phosphoric acid treatment of the tube, dissociation fractions of up to 40% have been reached in oxygen containing trace amounts of H_2 and H_2O. Considerable data have been obtained under a variety of O atom source conditions. Interpretation of these data is in progress.

8.   *Improved Master/Simple Codes for D, E, F Regions—W. Ali, NRL (Work Unit 11).*

The NRL Master Code which describes the ionization and de-ionization of the E and F regions of the ionosphere under disturbed conditions (nuclear burst) has been updated. A series of de-ionization runs has been performed with the old set of the reaction rates. These are now being analyzed. A corresponding series of de-ionization calculations with the most recent and current reaction rates will be made in the near future. These two sets will be compared and the impact of the reaction rates will be assessed in a forthcoming report.

B.   SUBTASK S99QAXHD028
"Theoretical Investigations of Ionizing Mechanisms in the Upper Atmosphere"

1.   *Theoretical Aspect of Ion—Ion Laboratory Measurements—F. Smith, SRI International (Work Unit 45).*

Three papers were completed, prepared for publication, and submitted to The Physical Review. These represent the combined results of work done under this project as well as under other sponsorship, mostly that of AFOSR.

a. W. H. Miller and F. T. Smith, "Semiclassical Perturbation Theory of Electron-Molecule Collisions."

b. A. P. Hickman and F. T. Smith, "Momentum Transfer in Electron-Polar Molecule Collisions: Results of Semiclassical Perturbation Scattering Theory."

c. D. Mukherjee and F. T. Smith, "Semiclassical Perturbation Theory of Electron-Polar Molecule Collisions: Total Excitation and Scattering Cross Section."

These pieces of work were also presented at the Tenth International Conference on the Physics of Electron and Atomic Collisions in Paris, France, July 21-27, 1977. In completing these papers a number of general formulas were derived for the semiclassical analysis of combined vibrational and rotational energy transfer in the collisions of charged particles with molecules or molecular ions. These will be directly applicable to the ion-ion neutralization problem for small cluster ions.

The first of these papers gives a general exposition of the semiclassical perturbation methods. In it, the procedure has been generalized to show how it can be used for vibrational excitation as well as rotational energy transfer. This provides the calculational procedure that now can be applied to the case of more complex cluster ions in which the transfer of energy to internal bending modes, as well as rotations, will be of crucial importance. The required calculations appear to be very economical in computer time even in the more complicated situations where several vibrational and rotational modes are involved.

The second paper describes specific applications to the calculation of rotational excitation cross sections and total scattering cross sections in the collisions of electrons with polar molecules. The third deals with momentum transfer cross sections in the electron-polar molecule collisions.

Approximations will be developed to simplify the calculation of the semiclassical expressions applicable to heavy particle collisions. This is a necessary preliminary to efficient calculations on specific cases of ion-ion neutralization.

Work has also been initiated on a general paper dealing with the current state of the theory for ion-ion neutralization as it applies to cluster ions. This paper will collect the principal conclusions with regard to the energy transfer and tidal excitation model of capture and subsequent stabilization and will summarize the semiquantitative conclusions that can be drawn without extensive detailed calculations.

2. *Reaction Rate Sensitivity Assessments—M. Bortner, T. Baurer, GEMSD (Work Unit 48).*

M. H. Bortner and T. Baurer met with the COR at DNA Headquarters in January 1977 to plan activities of the DNA Special Ad Hoc Panel Number 2. Subsequently, M. H. Bortner conferred with panel members and others related to the work of the panel. The substance of these talks and conclusions follow.

In the ELF/VLF range, the status as of January was that M. Scheibe (MRC) was to provide a set of Effective Rate Coefficients (ERCs) to E. C. Field, Jr. (PSRC)[*] for the purpose of carrying out further simulation calculations. In addition, W. Moler (NOSC)[+] was to add WEPH-VI to his program. Subsequent to Bortner's trip, Scheibe did provide the required information to Field, and Field in turn modified his program accordingly, planning to carry out calculations based on directions of the panel meeting being planned for May. Also, Moler completed the addition of WEPH-VI to his program and was awaiting the results of the May meeting for further direction of his efforts.

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[*]Pacific Sierra Research Company

[+]Naval Ocean Systems Center, formerly NELC.

In the HF range, at the time of Bortner's trip, preliminary input conditions were chosen for calculations in both the D and E/F regions, and tentative plans were formulated for W. S. Knapp (G.E.–TEMPO) to do D-region vertical-profile absorption calculations using WEPH-VI alone. Some of these were then to be confirmed by computation using a coupled NUCOM/WEPH-VI code, providing the coupling could be effected. In the E/F region, Bortner was to select limits of variation for three critical reactions (see below under UHF), after which G. Smith (SRI) would carry out appropriate runs varying the E/F chemistry. These tentative plans were the subject of much subsequent telephone discussion and criticism, during which it developed that the planned coupling of NUCOM with WEPH-VI might be more difficult than had initially been thought. It was agreed, after further communication on the matter, that final decision on a course of action must await the conclusions of the May Panel meeting.

In the UHF range, at the time of Bortner's trip, it was agreed that variations in the chemical-kinetic parameters for three critical reactions would be selected for use both in the HF (E/F region) and in the UHF. The three critical reactions are:

$$N^+ + O \rightarrow N + O^+ \tag{1}$$

$$O^+ + N_2^{\ddagger} \rightarrow NO^+ + N \tag{2}$$

$$N(^2D) + O \rightarrow NO^+ + e \tag{3}$$
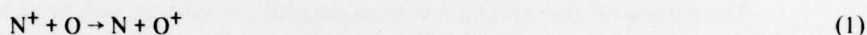
It was also agreed that the ROSCOE code would be used, in its unclassified version, for UHF calculations to be carried out by Scheibe. Subsequently, some trial runs were being carried out, the results of which were not yet available.

A set of 24 AIRCHEM code outputs with day and night conditions in the D region, times up to 10,000 sec post-burst, and varying Q_0 and N_0, was supplied by J. M. Heimerl (BRL). One of these runs was examined in some detail, in order to ascertain the dominant individual ion-ion recombination processes determinant of α_i (ion-ion recombination ERC) dependence as set forth by E. Field of PRC, Inc. The run thus examined was a daytime run at 60 km altitude, for which $Q_0 = 10^8$ and $N_0 = 10^{11}$. Results were in general agreement, insofar as dominant species and dominant ion-ion recombinations were concerned, with those reported by Heimerl for the same run. In addition, the dominant ion-electron dissociative recombinations contribution to α_d (dissociative recombination ERC) were also examined to discover the comparative effectiveness as deionization mechanisms of ion-electron as opposed to ion-ion processes, as a function of time. The usefulness of such a determination would lie in its specification, potentially, of separate time-frames within which one or the other process would dominate; if ion-electron processes should turn out to be dominant during an appreciable period, and given the relative insensitivity of ELF/VLF propagation to uncertainties in dissociative recombination kinetics as opposed to ion-ion kinetics, one might then be able to specify such a period as one for which relatively reliable communications might be anticipated. It turned out that, for the conditions of the run considered, deionization was dominated by ion-electron processes over ion-ion processes by at least an order of magnitude in rates during at least the first 1000 seconds post-burst. The cross-over in relative magnitudes occurred at about 7100 seconds, or not quite two hours post-burst. The tentative conclusion is that ELF/VLF communications can operate relatively free of uncertainty effects for at least the first 15 minutes or so post-burst, with increasing difficulty airsing from uncertainty thereafter up to almost two hours post-burst, and be thereafter completely overcome by uncertainty effects, at least under the conditions of the run examined. Similar examination of other AIRCHEM runs is under consideration pending direction from the May Panel meeting.

Pursuant to recommendations of Panel Number 2, a complete updating of Chapter 24, "Summary of Suggested Rate Constants," was concluded, and the final writeup was completed and submitted to DASIAC. The purpose of the Panel recommendations was to bring to bear within the various communications codes the very latest and best knowledge relating to the applicable chemical kinetics. In addition, inputs for a rewriting of Chapter 8, "Data-Gathering Methods Based on Theoretical Analysis," were received from H. H. Michels (UTRC) and from F. T. Smith (SRI) for editing and consolidation. Contacts were maintained with sources of input needed for the updating of Chapters 11 ("Atmospheric Radiative Processes in the Infrared") and 13 ("Photochemical Processes: Solar Photoionization and Photodissociation Rate Constants and Ultraviolet Intensities").

A. W. Ali, of NRL, has offered to undertake the updating (in cooperation with R. H. Kummler of Wayne State University) of Chapter 20 ("Excitation and Deexcitation Processes"), a chapter to which Ali had contributed rather heavily at the time of its first writing.

A meeting of Panel Number 2 (Sensitivity Assessment Panel) was arranged and (on 24-25 May) held at G.E.—TEMPO, Santa Barbara, California, under the chairmanship of M. H. Bortner.
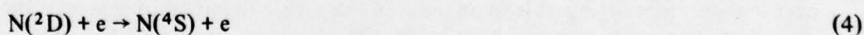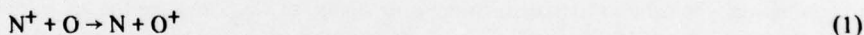
The purpose of the meeting was to summarize the work in each range of propagation frequencies of interest and to provide direction appropriate to the objectives of the panel.

Proceedings and conclusions of the panel meeting were summarized in a memorandum circulated to the COR and all panel members.

It was concluded that ELF/VLF propagation predictions are primarily affected by the ion-ion recombination kinetics, and secondarily by electron detachment processes. Improved ion mobility and collisional frequency data are needed in the further analysis of ELF/VLF phenomena. HF propagation predictions in the D region are significantly affected by both the dissociative recombination kinetics and electron detachment processes. Prediction of HF and UHF propagation in the E and F regions is influenced by the kinetics of four specific reactions: equations (1), (2), (3) and the electron collisional deexcitation of $N(^2D)$.

Plans for and recommendations of additional computations, experiments, and data assessments were set forth, with a view to minimizing critical chemical kinetics uncertainties and improving the understanding of the relevant chemical kinetics. A report of the proceedings of the meeting is soon to be published.

It had been reported at the meeting that four particular reactions are considered critical to the determination of uncertainty in HF propagation through the E and F regions, and in UHF propagation. These are:

$$N^+ + O \rightarrow N + O^+ \tag{1}$$

$$O^+ + N_2^\ddagger \rightarrow NO^+ + N \tag{2}$$

$$N(^2D) + O \rightarrow NO^+ + e \tag{3}$$

$$N(^2D) + e \rightarrow N(^4S) + e \tag{4}$$

Four individual members of the panel were assigned to prepare informal reports to the panel, in writing, on these four reactions. T. Baurer, of GEMSD, was one of those so assigned, to the third reaction listed.

The information developed on each of these is as follows:

(1)   W. Swider concluded, from an analysis of available cross-section data, that the Handbook value of 10^{-12} cm^3 sec^{-1} is "rather reasonable." Where N^+ is in the (^1S) state and O^+ is in the (^2P), $k = 10^{-9}$ cm^3 sec^{-1}.

(2)   M. Heaps reported that experimental data exist where $T_v \gtrsim 1000K$ (i.e., $v \geqslant 2$) and $T_k = 300K$, and where $v = 0$ and $T_k \gtrsim 800K$, but not where both T_v and T_k are elevated in the range $1000-6000K$. He suggested as lower limits:

$$k = 1.2 \times 10^{-12} (T/300)^{-1} \text{ where } T < 750K, \text{ and}$$

$$k = 8 \times 10^{-14} (T/300)^2 \text{ where } T > 750K, \text{ for}$$

$T = T_v$ or T_k. More experimental data are needed.

(3)   T. Baurer developed an expression, based on a detailed-balanced calculation, as follows:

$$k = (6.9 \pm 1.7) \times 10^{-12} \left(\frac{T}{300} \right)^{(0.4^{+0.2}_{-0.1})} \exp[-5000 \pm 500/T]$$

where $T = 300-1300K$. An alternative expression was subsequently suggested by A. W. Ali, based on a similar computation but starting from different premises:

$$k = 4.8 \times 10^{-16} \left(\frac{T}{300} \right)^{-0.4} T[1.4 + 1.2 \times 10^{-4}T + 1.4 \times 10^{-8}T^2] \cdot \exp(-5000/T),$$

said to be valid at $T = 1000-6000K$. Attempts are in progress to reconcile the differences between these.

(4)   A. W. Ali reported a variety of rate constant values, varying with the nature of the collision partner, and with the references cited. In general: where $M = N_2$, k has an upper limit of about 10^{-14} cm^3 sec^{-1}; where $M = NO$, k is the order of 10^{-10} cm^3 sec^{-1}; where $M = O$, $k = 1.8 \times 10^{-12}$ cm^3 sec^{-1}; and where $M = e$, k varies with T_e, between 0.6 and 2.9×10^{-9} cm^3 sec^{-1} in the range $T_e = 0.1-5.0$ eV.

C.   **SUBTASK S99QAXH1002**

"Atomic and Molecular Physics of IR Emissions."

1.   Chemistry and Spectroscopy of Optical Emitters–D. Snider, F. Niles, R. O. Olsen, J. Randhawa, AASLNM (Work Unit 41).

13 rocket flights and 6 balloon flights were performed between 14 June and 27 June 1977. The objectives were to:

   a.   Obtain measurements of the electrical and thermodynamic structure of the D region during periods of enhanced infrared emission, for the purpose of determining its cause.

   b.   Obtain measurements ot the ozone concentration, electrical, and thermodynamic structure during twilight and high sun periods, for the purpose of validating nuclear effects codes. A summary of the instrumentation and relevant flight parameters is given below. The data are currently being analyzed.

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SUMMARY OF ROCKET AND BALLOON LAUNCHES
DURING COSMEP V – JUNE 1977

DATE	TIME (UT)	VEHICLE	PAYLOAD	ALTITUDE (KM)	REMARKS
14 June 1977	2124	Balloon (small)	Mast O_3 Sonde	0–29	Good temperature–wind, humidity and O_3 data.
15 June 1977	1502 2201	Balloon (2mcf)	3 IR Radiometers	29	Everything appears to have worked but there is some question about the data obtained with the new IR Radiometers.
15 June 1977	1720	Super Loki	Blunt Probe	75.7–22.0	Conductivity data obtained were noisy–may require filtering before analysis.
15 June 1977	1837	Super Arcas	Chemiluminescent Ozone (UTEP)	Low	Rocket induced failure–low apogee–TM lost at expulsion–radar could not lock on–some evidence of chute damage at expulsion.
15 June 1977	1946	Super Loki	Datasonde	70–20	Good winds and temperature.
15 June 1977	2115	Super Loki	Blunt Probe	74.7–20.0	Good conductivity data obtained.
16 June 1977	1855	Balloon (small)	Mast O_3 Sonde	0–31.2	Good data.
16 June 1977	2100	Super Loki	Space data O_3	60.4–15.0	Good O_3 and wind data.
21 June 1977	0900	Super Loki	Space Data O_2	69.3–16	Partial data–PM tube signal too high at first part of flight–may have been due to light leak!
21 June 1977	1000	Arcas	UTEP O_3	44.4–13.0	Good data.
21 June 1977	1100	Super Loki	Datasone	~70	Bead Thermistor failed.
21 June 1977	1141	Super Loki	Datasonde	70.0–21.0	Good temperature and winds from 63.0 KM, no density due to lack of conjuctive RAOB.
21 June 1977	1307	Arcas	Gerdien Condenser	?	Failed to expell properly–no track. We had some trouble with the ball bearings but this should not have caused the problem.
21 June 1977	1420	Balloon (small)	Mast O_3 Sonde	0–30.5	Good data.
24 June 1977	1755	Balloon (small)	Mast O_3 Sonde	0–31.9	Good data.
27 June 1977	1945	Arcas	Gerdien	61–0	Payload separated from starute–no data obtained.
27 June 1977	1830	Super Arcas	UTEP O_3	83.7–13	Good data.
27 June 1977	2030	Super Loki	Datasonde	76.8–20.0	Good temperature and winds from 62 KM.
27 June 1977	2216	Balloon (small)	Mast O_3 Sonde	0–26.4	Good data.

2.   *UV and VUV Photoabsorption and Photoionization Investigations—R. Huffman, AFGL (Work Unit 42).*

Classified reports on the UV fireball emission lines have been obtained. Various data inputs required to assess degradation of satellite communications by the UV fireball were discussed with Dr. Irving Kofsky. In addition, discussions have been held with the Handbook editors concerning the geophysical inputs to photodissociation calculations to be done for the DNA Reaction Rate Handbook. Agreement was reached on altitude limits, molecules of interest, solar flux, latitude, solar zenith angle, and atmospheric model to be used in this work.

Naturally occurring ultraviolet and visible radiation allows passive observation techniques to be developed to investigate ionospheric characteristics of interest to DNA. The radiation is primarily associated with oxygen ion-electron recombination and related reactions. Further investigation into these techniques has been made, primarily in collaboration with Dr. I. Kofsky. Possibilities include peak ionospheric electron concentration and altitude, spatial imaging of ionospheric irregularities, and observation of auroral regions under sunlit conditions.

3.   *Reactions of Excited Atmospheric Gases—F. Kaufman, University of Pittsburgh (Work Unit 44).*

The paper which describes work on the excitation and lifetime of NO_2 near 600 nm has appeared in J. Chem. Phys.[1] It shows that the perturbed $^2B_2$ state of NO_2 is involved almost exclusively and it essentially removes the "lifetime anomaly" for that spectral region. Further experiments have now clarified the collisional quenching processes following tunable dye laser or fixed frequency laser excitation. These experiments involve measurement of the fluorescence spectrum as a function of NO_2 pressure or of helium or hydrogen pressure at fixed NO_2, all in the millitorr range. Furthermore, the temporal decay of fluorescent radiation was measured at specific frequencies, either in the banded or "continuous" part of the spectrum, again as a function of pressure.

In contradiction to recent claims [Butler et al., J. Chem. Phys. 62, 815 (1975)] that banded and "continuous" features of the NO_2 fluorescence spectrum are collisionally quenched with equal efficiency, we have now shown that banded features are quenched about six times faster, that at higher pressure the "continuum" shows the expected "growing-in" of intensity by vibrational cascade, and that the "step-ladder" mechanism of vibrational relaxation in the perturbed excited state, originally proposed by us, is able to explain the data satisfactorily. For M = He, the effective quenching probability is about five times lower than for NO_2 itself, in agreement with comparable data for other small molecules. Quenching experiments with other M-gases are now under way and a detailed mechanism of the relaxation process is being tested by computer calculations. A publication is in preparation.

A paper which describes the modeling and infers the line-shape parameters of vacuum UV resonance lamp emissions has been accepted for publication in J.Q.S.R.T.[2] Its results on the dependence of effective Doppler emission temperatures of O- and N-lamps on gas pressure and on RF or microwave power should be useful in laboratory as well as field (rocket, satellite) applications.

Laboratory studies on $N(^2P)$ reactions were then initiated using resonance fluorescence detection in a stainless steel fluorescence cell mounted at the entrance slit of a 0.5 meter VUV mono-

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[1]Fluorescence Lifetime Studies of NO_2: I. Excitation of the Perturbed $^2B_2$ State Near 600 nm, V. M. Donnelly and F. Kaufman, J. Chem. Phys. 66, 4100 (1977).

[2]Characteristics of OI and NI Resonance Line Broadening in Low Pressure Helium Discharge Lamps, W. T. Rawlins and F. Kaufman, submitted to the J. Quant. Spectrosc. and Radiat. Transfer, April 1977 (in press).

chromator. A detection limit of about 10^9 cm^{-3} was attained, about 100 times better than that using resonance line absorption as in our earlier studies. $N(^2P)$ studies are complicated by the fact that the strong radiative transitions from both $N(^2D)$ and $N(^2P)$ have a common upper state so that excitation at either wavelength (149.5 or 174.5 nm) will produce fluorescence at both. A Supersil window whose cut-off is near 16 nm was therefore placed between the microwave lamp and fluorescence cell. This isolates the $N(^2P)$ line and makes possible the sensitive detection at 149.5 nm where the scattered light intensity is negligible. Experiments in flowing Ar with small amounts of added N_2 in which the discharge was moved from 10 to 40 cm upstream of the detector showed pseudo-first order decays. Such decays at Ar pressures of 5 to 15 torr showed that surface deactivation of $N(^2P)$ was very rapid (~unit efficiency). From the slope and intercept of the plot of kp vs. p^2 the diffusion coefficient of $N(^2P)$ in Ar was found to be about 200 cm^2 sec^{-1} at 1 torr and k_Q for Ar was found to be less than or equal to 4×10^{-16} cm^3 sec^{-1}. The $N(^2P) + O_2$ reaction is now under investigation. This will be followed by a study of the $N(^2D) + O$ reaction which is both aeronomically and kinetically of great interest.

Vibrational relaxation processes of highly excited diatomics such as HCl[‡] in v = 1 to 7 continue to be investigated by infrared chemiluminescence in a fast flow system. The effects of energy resonance, dipole moment, dispersion and chemical forces are elucidated through a series of quenching experiments with different collision partners such as CO_2, CH_4, SF_6, CH_3Cl, CH_3F, and HCl(v=0). The resonance effect is clearly shown in the comparison of SF_6 and CH_4 where the latter is about an order of magnitude faster, presumably because of its high C-H frequencies. Both CH_3Cl and CH_3F are 5-10 times more efficient than CH_4 and CH_3F seems to be slightly faster than CH_3Cl. Because of an oversimplified model used in this analysis the absolute magnitude of the quenching rate constants may be somewhat in error, but their relative magnitudes are reliable. A large matrix of k_Q^v values for v = 1 to 7 and for about 10 quencher molecules is in preparation.

PART II–ABSTRACTS OF RELEVANT REPORTS

1. *Photodissociation of NO⁺(NO) and NO⁺(H₂O)–J. A. Vanderhoff, Ballistic Research Laboratory, Aberdeen Proving Ground, MD 21005.*

Report No. BRL 1994
July 1977

A drift tube mass spectrometer coupled with ion laser and ion laser pumped tunable dye laser photon sources has been used to measure the thermal energy (300K) photodissociation cross sections for two positive ion clusters, nitric oxide clustered with the nitric oxide ion and water clustered with the nitric oxide ion. Measurements were made spanning a photon wavelength range from 799 to 350 nm. The absolute photodissociation cross sections for nitric oxide clustered with the nitric oxide ion were found to vary smoothly with photon wavelength attaining a maximum value of 2×10^{-17} square centimeters at ~650 nm decreasing at both longer and shorter wavelengths. In addition, coupling of clustering reactions into the photodissociation cross section appeared under a variety of conditions.

Photodissociation cross sections for water clustering with the nitric oxide ion were found to be small or zero. Upper limits of ~1×10^{-19} square centimeters were obtained for these cross sections.

2. *Selected Neutral Species Profiles, 0-100 km–F. E. Niles and J. M. Heimerl, Ballistic Research Laboratory, Aberdeen Proving Ground, MD 21005.*

Report No. BRL MR 2767
July 1977

Daytime and nighttime concentration profiles have been assembled for the following neutral species: CO, CO_2, H, H_2, H_2O, H_2O_2, HNO_2, HNO_3, HO, HO_2, N, $N(^2D)$, NO, NO_2, N_2, N_2O, O, $O(^1D)$, O_2, $O_2(^1\Delta)$, $O_2(^1\Sigma)$ and O_3. Values for each species concentration are given in 5 km intervals for the altitude range 0–100 km.

3. *Negative Ions in CO₂–T. D. Fansler, L. M. Colonna-Romano, and R. N. Varney, Ballistic Research Laboratory, Aberdeen Proving Ground, MD 21005.*

Report No. BRL 1963
February 1977

Reaction rate coefficients for negative ions in carbon dioxide have been investigated in a drift tube by analysis of time-of-arrival spectra. Collisional detachment of electrons, clustering of the negative atomic oxygen ion to carbon dioxide, collisional dissociation of the carbon trioxide ion, and electron dissociative attachment have been studied at low pressure and over an order of magnitude range of the ratio of electric field to neutral number density (E/N), starting slightly above thermal. Changes of gas temperature have been shown to act to shift the reaction equilibrium in the same sense that changes in E/N do.

4.   *Nitrogen Dioxide Absorption Coefficients at High Temperatures*—D. E. Paulsen, R. E. Huffman, *Air Force Geophysics Laboratory, Hanscom AFB, Massachusetts 01731.*

Report No. AFGL-TR-76-0240
October 1976

The absorption coefficient of nitrogen dioxide, NO_2, is used in models of the fireball resulting from atmospheric nuclear detonations. This report gives values for the absorption coefficient obtained at wavelengths between 380 and 760 nm and at temperatures between 669 and $1313^O K$. The absorption coefficient varies from a maximum of about 10 cm^{-1} near 400 nm to about 0.1 cm^{-1} at the longest wavelength observed. The results agree with previously published data, which were available for only a few wavelengths, and provide a comprehensive data set over the temperature and wavelength regions studied. Comparison of these results is made with NO_2 thermal emission intensities.

5.   *Cross Section Measurements for Photodetachment or Photodissociation of Ions Produced in Gaseous Mixtures of O_2, CO_2, and H_2O*—R. A. Beyer, J. A. Vanderhoff, *Ballistic Research Laborabory, Aberdeen Proving Ground, MD 21005.*

Report No. BRL 1922
September 1976

A drift tube mass spectrometer coupled with a continuous laser photon source has been used to study photodissociation of thermal energy positive ion clusters. Absolute photodissociation cross sections have been measured for the singly charged positive ion of molecular oxygen clustered to one and two water molecules, clustered to molecular oxygen, and clustered to one carbon dioxide molecule. Upper limits have been established for the photodissociation cross sections of the atomic hydrogen positive ion clustered to one through four water molecules. All of these measurements have been made at room temperature and for low field conditions (10 or 14.3 x 10^{-21} volt-square meter). Photon wavelengths ranging from 676.4 nm to 454.5 nm were studied.

The hydrated proton clusters were found to have small or zero cross sections. The single molecules of water and carbon dioxide clustered to the molecular oxygen cation have cross sections which behave similarly over part of the photon energy range. Near 2.60 eV both ions have cross sections approaching 6 x 10^{-22} square meter. The photodissociation of the molecular oxygen cation-carbon dioxide cluster produces a singly charged carbon dioxide cation photofragment. From the appearance of this fragment an upper bound on the dissociation energy of the molecular oxygen ion cluster to carbon dioxide was placed at 0.46 eV.

6.   *Values for Selected Collisional Dissociation Rate Coefficients of Positive Clustered Ions*—J. M. Heimerl, *Ballistic Research Laboratory, Aberdeen Proving Ground, MD 21005.*

Report No. BRL 1917
August 1976

Values of the rate coefficient, k_r, for 15 gas-phase, two-body, collisional-dissociation reactions involving positive cluster ion of aeronomic interest have been tabulated. These values have been cast into the form $k_r = A (T/300)^B \exp (C/T)$. Where possible, error bounds for the constants A, B, and C have been estimated.

7. *Reactions Between AlO_x and O Atoms—Arthur Fontijn, AeroChem Research Laboratories, Inc., P.O. Box 12, Princeton, N.J. 08540.*

Report No. RADC-TR-77-2
January 1977

Rate coefficients for the reactions $AlO + O \rightarrow Al + O_2$, $AlO_2 + O \rightarrow AlO + O_2$, $Al + SO_2 \rightarrow AlO + SO$ and $Al + NO + M \rightarrow AlNO + M$ from high-temperature fast-flow reactor (HTFFR) measurements are reported. $D(Al-O)$ was determined to be $\geqslant 126$ kcal mole^{-1}. Emission of chemiluminescence continua (280 nm to > 725 nm) in mixtures of atomic Al with (i) O atoms and (ii) N atoms occurs, via not yet elucidated addition mechanisms, with a rate coefficient of 10^{-12} to 10^{-11} ml molecule^{-1} sec^{-1}.

8. *Comments on the Solution of Coupled Stiff Differential Equations—M. D. Kregel and J. M. Heimerl, Ballistic Research Laboratory, Aberdeen Proving Ground, MD 21005.*

Report No. BRL 2769
July 1977

The K-method of integrating sets of ordinary differential equations is outlined. This algorithm employs a variable step size, third order predictor-corrector method. It is written to reduce truncation error and to maximize stability consistent with reasonable execution time. The K-method has been used to integrate equations with discontinuous driving functions and this algorithm conserves chemical balance within the machine round-off error. It has been applied to solve kinetics problems in aeronomy and examples are taken from that field.

9. *Ionic and Neutral Reactions Relevant to Communications and Ionospheric Processes—Wade L. Fite and Frederick Kaufman, Department of Physics and Astronomy, University of Pittsburgh, Pittsburgh, PA 15260.*

Report No. P-13285-C
August 15, 1977

A brief review of data on identifying important ions following associative ionization processes of U and Th has indicated that UO_2^+ and ThO_2^+ are probably the respective terminal ions in atmospheric processes. These ions are either formed directly or are produced by the ion-molecule reaction $MO^+ + O_2 \rightarrow MO_2^+ + O$. Two contributions were made to the field of neutral-neutral processes: (1) To aid vibrational relaxation measurements on HX species, a pre-titration flow tube system was built which provides simple and accurate measurements of 1-atom densities. (2) A tunable dye laser wavelength narrowing attachment was put into operation which makes possible the measurement of OH densities at $\geqslant 10^8$ cm^{-3}. This has been used to determine the rate constant of an atmospherically important reaction of the HO_2 radical.

10. *Collisional Dissociation and Structural Properties of Atmospheric Negative Ions—J. T. Moseley, SRI International, Molecular Physics Center, 333 Ravenswood Avenue, Menlo Park, CA 94025.*

Final Report
June 1977

The transport properties, collisional dissociation, and photodissociation of N_4^+ have been measured. The photodissociation cross section of CO_3^- has been interpreted to yield structural information on this ion, including vibrational frequencies, bond energy, and electron affinity. A detailed study of the photodissociation of $O_2^+(a^4\Pi_u)$ has been made, leading to the discovery of a new state, $f^4\Pi_g$, and of new techniques for high resolution spectroscopy of ions.

11.   *The Effects of Uncertainties in the Two-Body Ion-Ion Recombination Coefficient Upon Computed Ion Distributions in the Stratosphere and Mesosphere—Joseph M. Heimerl, Ballistic Research Laboratory, Aberdeen Proving Ground, MD 21005.*

Report No. BRL 1972
March 1977

A version of the AIRCHEM code (BENCHMARK-76) has been used to study the sensitivity of the daytime ionic populations to decade changes in selected values of the two-body ion-ion recombination rate coefficient over the altitude range 30–80 km, inclusive. At one extreme, computed ionic populations change by as much as a factor of two in isolated cases. At the other extreme much smaller changes are computed.

12.   *Investigation of Ion-Ion Recombination Cross Sections—F. T. Smith and A. P. Hickman, SRI International, Molecular Physics Center, 333 Ravenswood Ave., Menlo Park, California 94025.*

Report No. AFGL-TR-77-0055
February 1977

This is a brief review of the chief theoretical methods for estimating atomic and molecular collision processes for use in atmospheric and ionospheric modeling. It is intended for inclusion in the DNA Reaction Rate Handbook. The principles of the most important techniques are mentioned, and reference made to more complete treatments. Problems include reactive and non-reactive collisions, energy transfer, ionization and neutralization.

AUTHOR–CORPORATION INDEX